LLNL-CONF-425662

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Effects of Anisotropic Coherency Strains on Intercalation in Phase-Separating Crystals

L. G. Stanton, M. Z. Bazant

March 12, 2010

American Physical Society - March Meeting 2010
Portland, OR, United States
March 15, 2010 through March 19, 2010

Disclaimer

Effects of Anisotropic Coherency Strains on Intercalation in Phase-Separating Crystals

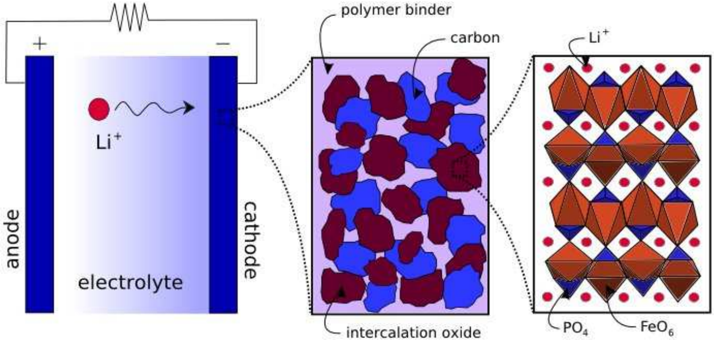
Liam Stanton*
Lawrence Livermore National Laboratory

Martin Z. Bazant
Massachusetts Institute of Technology

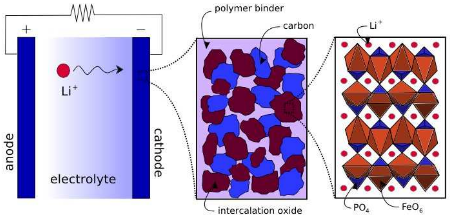
APS March Meeting
March 15, 2010

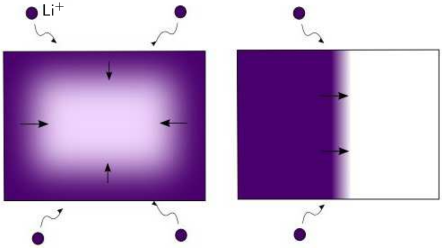
*This research was supported by NSF RTG grant DMS-0636574 and partially under the auspices of the U.S. Department of Energy by LLNL under Contract DE-AC52-07NA27344. [*LLNL-CONF-425662*]

Li^+ intercalation in Li_xFePO_4



Li^+ intercalation in Li_xFePO_4





phase-field formulation

- order parameter

$$c = [\mathrm{Li}], \quad 0 < c < 1$$

- total free energy

$$\mathscr{F}[c] = \int_{\Omega} f(c, \nabla c, \ldots) d\mathbf{x}, \quad \mathbf{x} \in \Omega$$

G.K. Singh, G. Ceder, M.Z. Bazant (2008)

energetic contributions

$$\mathscr{F}[c] \approx \int_\Omega \left\{ f_0(c) + \frac{1}{2}\nabla c \cdot \mathbf{K}\nabla c + \frac{1}{2}\mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

energetic contributions

$$\mathscr{F}[c] \approx \int_\Omega \left\{ f_0(c) + \frac{1}{2}\nabla c \cdot \mathbf{K}\nabla c + \frac{1}{2}\mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

$$f_0(c) = ac(1-c) + k_B T \left[c \log(c) + (1-c)\log(1-c) \right]$$

energetic contributions

$$\mathscr{F}[c] \approx \int_\Omega \left\{ f_0(c) + \frac{1}{2}\nabla c \cdot \mathbf{K}\nabla c + \frac{1}{2}\mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

$$f_0(c) = ac(1-c) + k_B T \left[c\log(c) + (1-c)\log(1-c) \right]$$

(enthalpy of mixing)

energetic contributions

$$\mathscr{F}[c] \approx \int_{\Omega} \left\{ f_0(c) + \frac{1}{2}\nabla c \cdot \mathbf{K}\nabla c + \frac{1}{2}\mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

$$f_0(c) = ac(1-c) + k_B T \left[c \log(c) + (1-c)\log(1-c) \right]$$

(entropy of mixing)

energetic contributions

$$\mathscr{F}[c] \approx \int_\Omega \left\{ f_0(c) + \frac{1}{2}\nabla c \cdot \mathbf{K}\nabla c + \frac{1}{2}\mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

$\mathbf{K}$ – symmetric, positive-definite tensor

(gradient penalty)

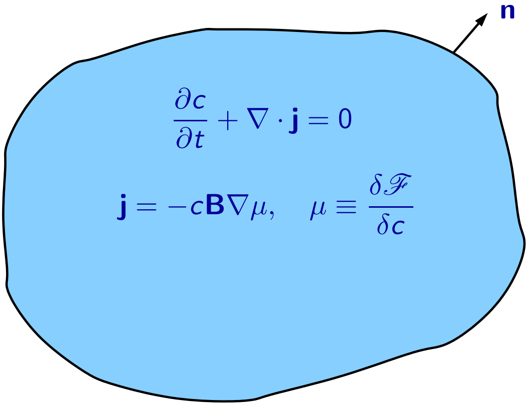
energetic contributions

$$\mathscr{F}[c] \approx \int_\Omega \left\{ f_0(c) + \frac{1}{2}\nabla c \cdot \mathbf{K}\nabla c + \frac{1}{2}\mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

$$\mathbf{T} = \mathbf{CE}, \quad \mathbf{E} = \frac{1}{2}\left(\nabla\mathbf{u} + \nabla\mathbf{u}^T\right) - c\mathbf{M}$$

(elastic energy)

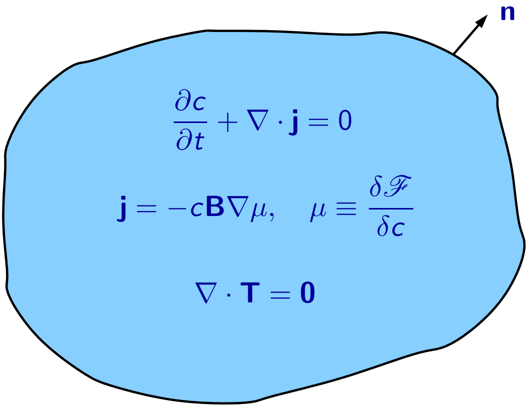
governing equations



$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

$$\mathbf{j} = -c\mathbf{B}\nabla\mu, \quad \mu \equiv \frac{\delta \mathscr{F}}{\delta c}$$

governing equations

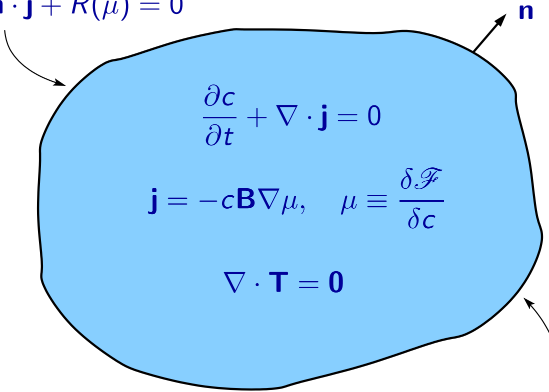


$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

$$\mathbf{j} = -c\mathbf{B}\nabla\mu, \quad \mu \equiv \frac{\delta \mathscr{F}}{\delta c}$$

$$\nabla \cdot \mathbf{T} = \mathbf{0}$$

governing equations



$$\mathbf{n} \cdot \mathbf{j} + R(\mu) = 0$$

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

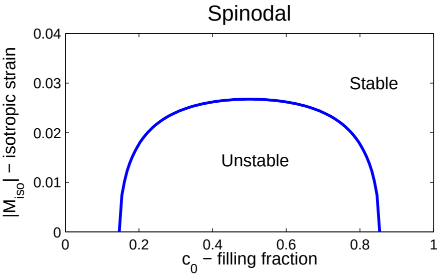
$$\mathbf{j} = -c\mathbf{B}\nabla\mu, \quad \mu \equiv \frac{\delta \mathscr{F}}{\delta c}$$

$$\nabla \cdot \mathbf{T} = \mathbf{0}$$

$$\mathbf{n} \cdot (\mathbf{T} + P\mathbf{I}) = \mathbf{0}$$

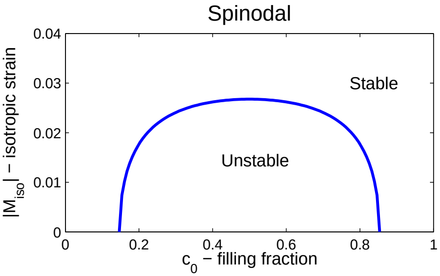
isotropic strain: $\mathbf{M} = M_{iso}\mathbf{I}$

LSA: $c(\mathbf{x}, t) = c_0 + \tilde{c}e^{\sigma t + i\mathbf{q}\cdot\mathbf{x}}, \quad \mathbf{u} = \tilde{\mathbf{u}}e^{\sigma t + i\mathbf{q}\cdot\mathbf{x}}$



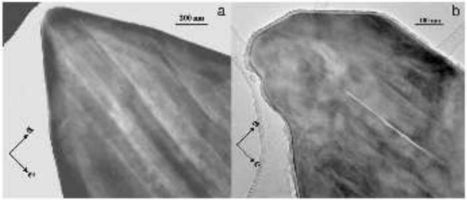
isotropic strain: $\mathbf{M} = M_{iso}\mathbf{I}$

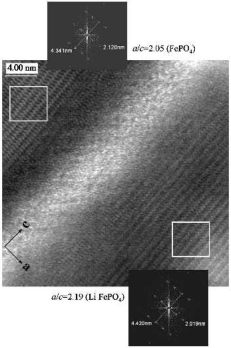
LSA: $c(\mathbf{x}, t) = c_0 + \tilde{c} e^{\sigma t + i\mathbf{q}\cdot\mathbf{x}}, \quad \mathbf{u} = \tilde{\mathbf{u}} e^{\sigma t + i\mathbf{q}\cdot\mathbf{x}}$



strain *suppresses* phase-separation

anisotropic strain

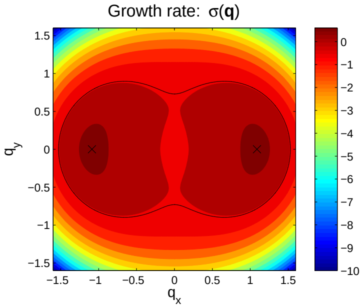




G. Chen, X. Song, T.J. Richardson (2006)

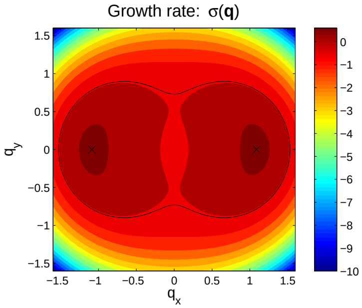
anisotropic strain

$$M_{11} = 0.05, \; M_{22} = 0.03, \; M_{33} = -0.02$$



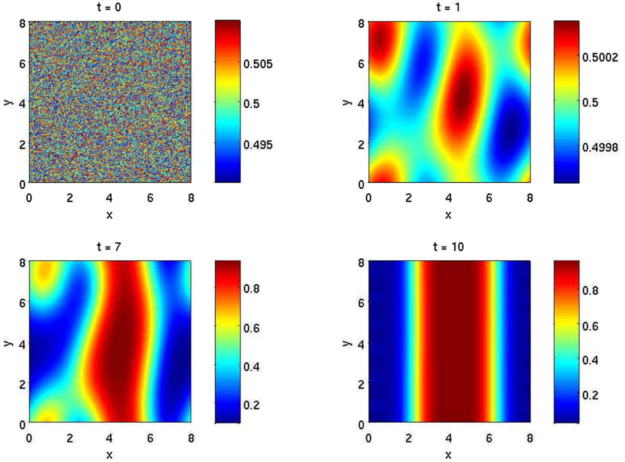
anisotropic strain

$$M_{11} = 0.05,\ \ M_{22} = 0.03,\ \ M_{33} = -0.02$$

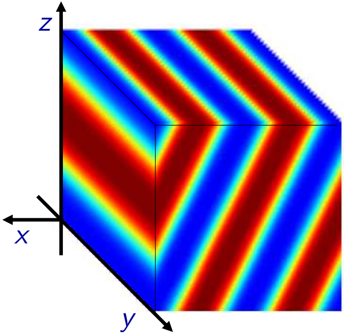


phase-separation occurs along direction of *largest* strain

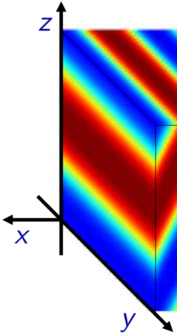
numerical simulations



numerical simulations



numerical simulations



skew induced by strain contraction

summary

- Extended model developed by Singh, Ceder and Bazant to include elastic effects from Li^+ intercalation in $LiFePO_4$
- LSA showed lattice mismatch strains to *suppress* spinodal decomposition (phase-separation)
- Phase-separation will occur along direction of *largest* strain with contraction induced skew
- Numerical simulations verify long-term dynamics

Thank You!